

Electron Transfer between Biphenyl and Biphenyl Anion Radicals: Reorganization Energies and Electron Transfer Matrix Elements

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ABSTRACT: Intermolecular electron transfer (ET) between the parallel benzene anion radical and neutral benzene is studied at the UHF/4-31G level. It is found that the diabatic activation energy remains almost invariant (14.2 kJ mol^{-1}) when d , the distance between the two parallel benzene rings, is $> 0.45 \text{ nm}$. The exponential fall-off of the ET matrix element, V_{rp} , with d is examined. On the basis of the calculated results of the ET matrix element for the system of two parallel benzenes, it is concluded that direct calculation of the ET matrix element, based on the two-state model, is more accurate than that based on the Koopmans theorem. *Ab initio* calculations are performed in the investigation of the ET reaction between biphenyl anion radical and neutral biphenyl. By using the Dunning's (9s, 5p)/(3s, 2p) basis set with polarization functions on all atoms (DZP), the reorganization energy for the gas phase intermolecular ET is shown to be $109.2 \text{ kJ mol}^{-1}$. Using the UHF/STO-3G method and direct calculation of the two-state model, V_{rp} values of $2.055 \text{ kJ mol}^{-1}$ and $0.429 \text{ kJ mol}^{-1}$ are obtained for cyclohexylenyl- and decalenyl-mediated ET systems. When we use the Koopmans theorem instead of the direct calculation, these V_{rp} values are shown to be 1.55 kJ mol^{-1} and $0.326 \text{ kJ mol}^{-1}$ for the two corresponding systems, respectively. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 597–603, 1999

Keywords: electron transfer; reorganization energy; electron transfer matrix element; electron-localized diabatic state

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Introduction

Metals, semiconductors, and insulators are represented in terms of band structures. For metals, the band is about half-filled with electrons and hence no activation energy is necessary for the generation of charge carriers. In contrast, the band is completely filled with electrons for both semiconductors and insulators, and therefore activation is required for the transition of electrons from the valence band to the conduction band to generate charge carriers. For this reason, doping is needed to generate charge carriers for the conducting organic polymers. The theoretical research on conducting polymers has been concerned mainly with radical and ionic sites, referred to as neutral radical and charged defects, respectively. To describe the movements of defects, the concept of solitary wave has been used mathematically. Such a concept is described as a *soliton* in the language of field theory. The radical defect is referred to as a neutral soliton, and the anion defect or the cation defect is referred to as a charged soliton.^{1,2} Many investigations of neutral and charged defects in conjugated polymers have been presented on the basis of quantum chemical Huckel calculations, which are known to have quantitative limitations. More sophisticated treatments of neutral and charged defects in various conjugated polymers, including *ab initio* calculations, have been carried out.^{3,4} Recently, the two-site model has been used for the investigation of interchain electron transfer (ET) in polyacetylene, and ET matrix element and other ET kinetic parameters have been investigated using quantum chemical *ab initio* calculation.⁵⁻⁷

Recently, there has been considerable interest in the kinetic study of ET reactions. When biphenyl is taken as the donor or the acceptor in an ET reaction, the reorganization energy is partly contributed from the torsion motion of the molecule. ET rate constants between the biphenyl anion radical and a series of acceptors have been measured experimentally.⁸ To examine the influence of biphenyl torsion motion upon ET reorganization energy, experiments have been performed using both biphenyl and fluorene as the electron donors,^{8a} because the former will undergo torsion of about 45°, whereas the latter remains planar in the ET process due to the existence of the tetrahedral carbon. A reorganization value of 0.13 eV of en-

ergy contributed from the interring torsion has been obtained from the difference in ET rate constants in these two cases.^{8a}

The purpose of the present study is to investigate theoretically the reorganization energy and the ET matrix element for the spacer-mediated ET from the biphenyl anion radical to the neutral biphenyl. In describing the transition state of the self-exchange reaction, we employed the linear reaction coordinate and the electron-localized initial-guess-induced SCF technique. In comparing different methods for calculating the ET matrix element, the ET reaction between parallel benzene anion radical and neutral benzene has been investigated and the distance dependence of the ET matrix element is discussed.

Electron Transfer between Parallel Benzene Anion Radical and Neutral Benzene

The mechanism of interchain conductivity of poly(*p*-phenylene) (PPP) can be described by the interchain hopping of bipolaron as shown in Figure 1a. To realize the quantum chemical calculation for such conducting polymers, the ET between parallel acetylene and acetylene anion radical,⁶ and the ET between parallel allyl and allyl anion radical were investigated by Rodriguez-Monge et al.⁵ The conductivity of a polymer is essentially an ET process. An excess electron or a hole appears after the virgin polymer has been doped. In this work, we take benzene, the monomer of PPP, into account, and investigate the electron transfer between parallel benzene anion radical and neutral benzene. In our calculations for the gas phase ET reaction (Fig. 1b, the distance, *d*, between the donor and the acceptor is assumed to remain constant.

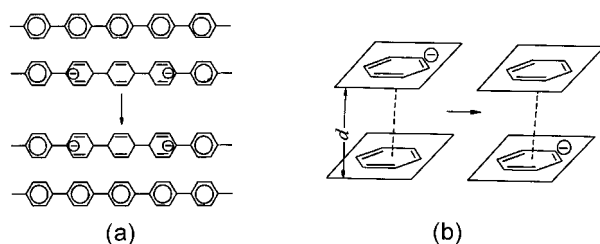


FIGURE 1. (a) Interchain hopping of bipolaron in PPP. (b) Scheme for the ET reaction between benzene anion radical and neutral benzene.

Marcus's theory⁹ has been used widely to investigate ET processes. According to transition state theory, the non-adiabatic ET rate constant for a self-exchange reaction can be expressed as^{9c,10a}:

$$k = \frac{V_{rp}^2}{h} \frac{\pi^{3/2}}{(k_B T E_c)^{1/2}} \exp(-E_c/RT) \quad (1)$$

where V_{rp} is the ET matrix element, h the Planck constant, k_B Boltzmann's constant, T the temperature, and E_c the diabatic activation energy. The ET between a benzene anion radical (C_6H_6)⁻ and a neutral benzene C_6H_6 is a self-exchange reaction (cf. Fig. 1b). We use Φ_r and Φ_p to denote the two electron-localized diabatic states. These two states can be expressed as two Slater determinants^{10b,c} and have the same energy at the crossing of diabatic potential surfaces. Linear reaction coordinates are employed in determining the transition state geometry,^{10a-d} that is:

$$Q_i = (Q_i^r + Q_i^p)/2 \quad (2)$$

where Q_i refers to the i th internal coordinate (bond length, bond angle, or dihedral angle), and r and p refer to the reactant and product, respectively. By defining $S_{rp} = \langle \Phi_r | \Phi_p \rangle$ and $H_{ij} = \langle \Phi_i | \mathbf{H}_e | \Phi_j \rangle$ ($i, j = r, p$, and \mathbf{H}_e is the electronic Hamiltonian), the ET matrix element can be written as¹⁰:

$$V_{rp} = (E_1 - E_0)/2 \\ = [H_{rp} - S_{rp}(H_{rr} + H_{pp})/2]/(1 - S_{rp}^2) \quad (3)$$

when the two-state model has been invoked. In eq. (3), E_0 and E_1 are the two adiabatic potential energies of the ground state and the first excited state, respectively.

On the other hand, the Koopmans theorem can be used to estimate the value of V_{rp} by calculating the transition energy from LUMO and the next lowest unoccupied molecular orbital (LUMO1) for the neutral system (C_6H_6)₂; that is^{5,6,11}:

$$\Delta = 2V_{rp} = \varepsilon_{\text{LUMO1}} - \varepsilon_{\text{LUMO}} \quad (4)$$

where Δ is the energy splitting factor at the crossing point, and ε is the eigenvalue of the canonical SCF MO.

We use the symmetry constraint of D_{6h} to perform the geometry optimization for neutral C_6H_6 , and use D_{6h} constraint and D_{2h} constraint to perform the geometry optimization for anion radical (C_6H_6)⁻ at the 4-31G level. For the system (H_6H_6)⁻, the D_{6h} constraint gives one optimized geometry with a minimum energy of -230.15434

a.u. whereas the D_{2h} constraint gives the other optimized geometry with an energy of -230.26627 a.u. Therefore, the D_{2h} benzene anion radical, because of its lower total energy, has been applied to form the donor-acceptor couple with the neutral benzene in the ET reaction.

For electron localization, we increase the distance between the donor and the acceptor with the optimized geometries of the neutral molecule and the anion, so that the SCF calculation gives a set of MOs in which an excess electron is entirely localized in the anion. With this set of electron-localized MOs to induce the UHF SCF calculations at the 4-31G level, we obtained the total energies, E_r , of the reactant and the E_{tran} of the diabatic transition state, at different donor-acceptor distances d (Fig. 2a). The transition state has been determined with eq. (2). The diabatic activation energy can be calculated using:

$$E_c = E_{\text{tran}} - E_r \quad (5)$$

From variation of E_r with d , we did not find a minimum of E_r along d . When $d \geq 0.45$ nm, E_c remains almost invariant at approximately 14.2 kJ mol⁻¹. When $d < 0.45$ nm, E_c decreases with the decreasing d . The results of the ET reaction between two parallel ethene molecules by Rodriguez-Monge et al.⁶ produced a similar conclusion that the ET activation energy is of approximately constant value of 6 kJ mol⁻¹ when d , the distance between the two parallel ethene molecules, is greater than 0.5 nm. In the determination of an ET matrix element V_{rp} , both eq. (3) and eq. (4) are used for comparison. Values of V_{rp} at different distances d are shown in Fig. 2b. It is widely believed that the relationship between V_{rp} and d can be described by^{9,12}:

$$V_{rp} = V_{rp}^0 \exp[-\beta(d - d_0)] \quad (6)$$

where V_{rp}^0 is the ET matrix element at $d = d_0$ and β is a constant. From Figure 2b one can see that these results, obtained by solving the secular equation of two states [eq. (3)], are more appropriate for fitting eq. (6), whereas eq. (4) fails to describe these results in the region of small d . To sum, the energy splitting between two MOs used in the estimation of V_{rp} is not much more reliable than the approach of direct calculation based on the two-state model. A least-square method has been applied to fit the constant β by transferring eq. (6) into the form of:

$$\ln V_{rp} = \ln V_{rp}^0 - \beta(d - d_0) \quad (7)$$

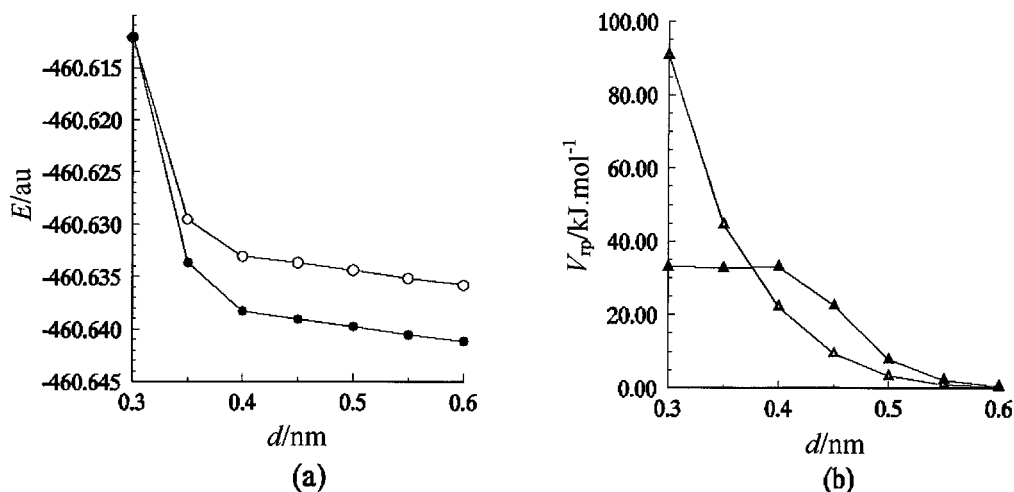


FIGURE 2. Total energy and ET matrix element at different donor-acceptor distances d . (a) The total energy, E_r (filled circles) of the reactant, and the total energy E_{tran} (open circles), of the diabatic transition state. (b) The ET matrix, V_{rp} . Open triangles designate those calculated using eq. (3), and filled triangles refer to those calculated using the splitting energy between LUMO and LUMO1 [cf. eq. (4)].

A linear fit for V_{rp} of direct calculation gives a value of 24.149 nm^{-1} for β ; that is:

$$V_{rp} = 4.5976 \times 10^5 \exp(-24.149 d/\text{nm}) [\text{kJ mol}^{-1}] \quad (8)$$

The correlation coefficient turns out to be -0.9966 .

ET between Spacer-Mediated Biphenyl Anion Radical and Neutral Biphenyl

Biphenyl, the dimer of PPP, is a typical system in the family of PPP oligomers. Its molecular structure, electronic properties, and reactivity have been studied intensively through MO calculations.^{13–17} For neutral biphenyl, we used both AM1 and *ab initio* calculations to investigate the torsion angle and the height of the rotational barrier. AM1 semiempirical method optimization gives a value of 44.0° for the torsion angle. On the other hand, UHF/4-31G optimization gives a torsion angle value of 45.1° , and the internal rotation has a barrier height of $17.64 \text{ kJ mol}^{-1}$ when the torsion angle changes from 45.1° to 0° . These results are consistent with those of experimental estimations and theoretical calculations by other researchers. For example, values of 44.74° for torsion angle and 13.5 kJ mol^{-1} for the internal rotation barrier height at the level of 6-31G have been obtained by Hafelinger et al.,¹⁶ whereas the 6-31G** calculation

performed by Tsuzuki et al.¹⁴ resulted in a larger torsion angle (46.26°), and MP2/6-31G*//HF/6-31G* calculation performed by the same investigators resulted in a value of $16.05 \text{ kJ mol}^{-1}$ for the barrier height.¹⁴ At the level of UHF/4-31G, we obtained C—C bond length between the two phenyl rings of 0.1486 nm , which is obviously more reliable than the 0.1462 nm obtained by AM1 calculations. In geometry optimization, a C_2 symmetry constraint has been applied.

At the level of UHF/4-31G, a planar structure for the biphenyl anion radical has been optimized. Such coplanarity for the biphenyl anion radical or the biphenyl cation radical has also been predicted by others.^{18,19} The C—C bond length between the two phenyl rings is 0.1472 nm . This value of bond length implies that the anion radical is more likely a π -system, because the conjugated π electrons force the C—C bond close to a double bond.

To investigate ET from the biphenyl anion radical to the neutral molecule, two ET systems have been designed, as shown in Figure 3. ET reactions between the biphenyl anion and a series of acceptors have been investigated experimentally in fluid solution by Miller et al.⁸ In this work, we optimize the geometries of biphenyl anion radical and neutral biphenyl, as well as the two spacers at the UHF/4-31G level, and then investigate the ET activation energies and ET matrix elements for the two ET reactions demonstrated in Figure 3.

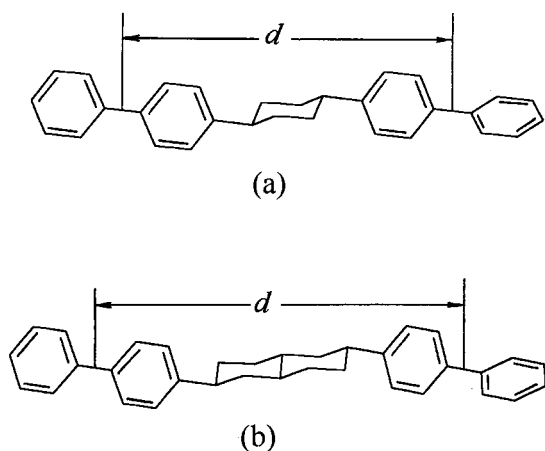
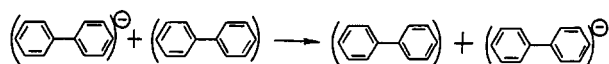


FIGURE 3. Self-exchange ET between the biphenyl anion radical (B^-) and natural biphenyl (B) mediated by (a) cyclohexylenyl (S_1) and (b) decalenyl (S_2). d is the distance between the mass centers of the donor and the acceptor.

Internal Reorganization Energy and Torsion Potential Barrier

The reorganization energy for a gas phase ET between the biphenyl anion radical and neutral biphenyl is different from the torsion barrier as the torsion angle varies from 45.1° to 0° , because changes of bond lengths and bond angles take place when the system varies from the twisted neutral molecule with the torsion angle of 45.1° to a coplanar anion radical. To calculate the reorganization energy, let us consider the intermolecular ET between the biphenyl anion radical and the neutral molecule (Scheme 1).



SCHEME 1.

We divide the internal reorganization energy into two parts: one from the torsion of the neutral biphenyl and the anion radical, and the other from the changes of all internal coordinates except the torsion motions. At the 4-31G level, we found that the total reorganization energy for ET (Scheme 1) is $111.39 \text{ kJ mol}^{-1}$. For neutral biphenyl, the energy barrier of the simple twist from 45.1° to 0° is $17.64 \text{ kJ mol}^{-1}$, as illustrated. For the biphenyl anion radical a simple torsion motion from 0° to 45.1° gives a value of $36.11 \text{ kJ mol}^{-1}$ for the barrier height, which is about two times higher than that of the neutral molecule. We found that these two parts contribute a total of $53.75 \text{ kJ mol}^{-1}$ to the internal reorganization of the intermolecular reaction (Scheme 1). Therefore, we may say that one half of the reorganization energy comes from the torsion motion of both donor and acceptor. Such a result means that neither the torsion motion nor the bond length and bond angle changes can be neglected in the estimation of the internal reorganization of an ET reaction, which contains biphenyl as the donor or the acceptor. One study⁸ experimentally estimated the contribution for the reorganization energy from the interring torsion of the biphenyl fragment to be 0.13 eV ($12.55 \text{ kJ mol}^{-1}$), which is lower than the directly calculated result in the present work for both biphenyl ($17.64 \text{ kJ mol}^{-1}$) and its anion radical ($36.11 \text{ kJ mol}^{-1}$).

For comparison we employ UHF/4-31G-optimized geometries to perform the internal reorganization energy calculation with different basis sets (UHF/4-31G, UHF/STO-3G, and UHF/DZP). These calculated reorganization energies are listed in Table I. It can be seen that the internal reorganization energy, λ_i , calculated using a STO-3G, is higher than that calculated with 4-31G and DZP basis sets by about 30 kJ mol^{-1} . Clearly, we should consider the DZP result more reliable. When a harmonic oscillator is employed to describe the symmetric double-well potential, the activation energy (E_c) is equal to $\lambda_i/4$. These values are also shown in Table I.

TABLE I. Internal Reorganization Energy (λ_i) and Activation Energy (E_c) for Gas Phase Intermolecular ET between Biphenyl Anion Radical and Neutral Biphenyl.

Basis set	UHF / STO-3G	UHF / 4-31G	UHF / DZP
λ_i (kJ mol^{-1})	143.53	111.39	109.21
E_c (kJ mol^{-1})	35.88	27.85	27.30

Spacer-Mediated ET between Biphenyl Anion Radical and Neutral Biphenyl

Two spacers, cyclohexylenyl and decalenyl, as shown in Figure 3, are isolately optimized at the RHF/4-31G level. In linking the donor and acceptor to the spacers, we use the originally optimized geometries at the appropriate positions (Fig. 3) and assume a value of 0.1533 nm for the C—C bond, which connects the donor (or acceptor) and the spacer. Similar to the case of the ET reaction between benzene anion radical and neutral benzene, the ET transition state is determined with the linear reaction coordinate [eq. (2)]. The spacers are assumed to be rigid. In determining the reorganization energy and ET matrix element, we performed the initial-guess-induced UHFSCF calculations at the STO-3G level for the two ET systems, as shown in Figure 3. The calculated results, including net charge, overlap integral between the two electron-localized Slater determinants Φ_r and Φ_p , etc., are given in Table II.

The cyclohexylenyl- or decalenyl-mediated ET between the biphenyl anion radical (B^-) and the naphthalene molecule (N) have been measured experimentally by Closs et al. Their results^{8b} for V_{rp} for these two ET systems, B^-S_1-N and B^-S_2-N , are given in Table II for comparison. Some similarity between B^-S-B and B^-S-N (S represents S_1 or S_2) can be predicted because of the negligible free energy change ($\Delta G^0 = -0.05$ eV)^{8c} for the B^-S-N system.

From Table II it can be seen that, in these two intramolecular ET systems, B^-S_1-B and B^-S_2-B , the activation energies, E_c , are almost the same and close to the UHF/STO-3G results given in

Table I. Such a similarity of activation energies in both the intermolecular and intramolecular ET reactions is reasonable because we assumed the changes of bond lengths and bond angles in the donor and acceptor fragments to be the same as in the intermolecular ET. This simplification is helpful in the theoretical calculation of an intramolecular ET in which a long chain intervenes between the donor and the acceptor. In the B^-S_1-B and B^-S_2-B ET systems, we can use the more reliable DZP values of E_c instead of the UHF/STO-3G results in further kinetic calculations. In comparison with experimentally fitted results of V_{rp} in the ET reaction between biphenyl anion radical and neutral naphthalene mediated with the same spacers,^{8b} the values of V_{rp} determined in the present work are acceptable if we neglect the contribution of solvents to V_{rp} .

All *ab initio* calculations were performed by using the HONDO95.6 package.²⁰

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TABLE II. Overlap Integral between Φ_r and Φ_p , ET Matrix Element (V_{rp}), Activation Energy (E_c), Net Charges (P_D and P_A) of Transition State, and Distance (d) between Two Mass Centers of Donor and Acceptor for ET Systems B^-S_1-B and B^-S_2-B ^a (Energies in kJ mol⁻¹).

Systems	E_c	S_{rp}	V_{rp}	P_D^b	P_A^c	d (nm)
$B^-S_1-N^d$			1.686 ^e			1.18 ^f
$B^-S_2-N^d$			0.407 ^e			1.40 ^f
B^-S_1-B	36.35	-5.399×10^{-3}	2.055 ^g (1.555 ^h)	-0.94	-0.06	1.287 ⁱ
B^-S_2-B	36.60	1.132×10^{-3}	0.429 ^g (0.326 ^h)	-0.95	-0.05	1.646 ⁱ

^a UHF/STO-3G results. ^b Net charge on donor. ^c Net charge on acceptor. ^d Cyclohexylenyl- and decalkenyl-mediated ET reactions between biphenyl anion radical and neutral naphthalene appear in ref. 8b. ^e Fitted from the experimentally measured rate constant.^{8b} ^f MM2 force field optimized results.^{8b} ^g ET matrix elements using eq. (3). ^h ET matrix elements using energy splitting between LUMO and LUMO1 in a neutral system [cf. eq. (4)]. ⁱ Distance between the two mass centers of the donor and the acceptor.

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